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(12) # EUROPEAN PATENT SPECIFICATION

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(54) **Catalytic distillation sytem.**

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EP-A- 0 448 884
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GB-A- 1 019 236

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Description

Field of the Invention

The present invention relates to a system for concurrently carrying out chemical reactions and separating the reactants and products by fractional distillation. More particularly, the invention relates to a catalytic distillation system in which a particulate catalyst is dispersed in and supported by a bed of hollow geometric shaped particles having openings through the surface.

Related Art

A new method of carrying out catalytic reactions has been developed, wherein the components of the reaction mixture are concurrently separable by fractional distillation. Several systems have been proposed and one commercially successful uses the catalyst as the catalytic distillation structure. Such a system is variously described in U.S. patents 4,215,011; 4,232,177; 4,242,530; 4,250,052; 4,302,356; 4,307,254; 4,336,407; 4,439,350; 4,443,559; and 4,482,775 commonly assigned herewith.

Briefly, the commercial structure described therein comprises a cloth belt with a plurality of pockets spaced along the belt and containing particulate catalyst material. The cloth belt with catalyst filled pockets is wound into a helix about a spacing material such as knitted stainless steel wire mesh, and these "bales" are loaded into a distillation column. Additionally U.S. patents 4,302,356, 4,443,559 and 4,250,052 disclose a variety of catalyst structures for this use.

Placing the particulate catalyst loose on standard distillation trays has also been proposed. See, for example, U.S. Pat. No. 4,215,011 and U.K. patents GB 2,096,603 and 2,096,604. The placement of the catalyst in the downcomers of standard distillation columns has been proposed as in U.S. patent 3,634,534. Fluidization of the catalyst on the trays has also been suggested as in U.S. patent 4,471,154. Some deficiencies of such fluidized beds were recognized in Chemiker Zeitung/Chemische Apparatur, vol. 90, no. 13, July 1966 and U.S. Pat. No. 4,215,011. Quang, et al, in U.S. Pat. No. 4,847,430 and Nocca, et al in U.S. Pat. No. 4,847,431 disclose loading the particulate catalyst on alternating trays of a distillation column and with a gas bypass about the catalyst loaded trays.

The use of solid glass beads to disperse and support a catalyst in a fixed bed has long been used, especially in pilot plants and bench scale reactors. See for example U.S. patent 4,918,244 wherein glass beads were used as a dispersant and support in a bench scale reactor distillation column.

Additionally the use of containers filled with particulate catalyst has been proposed in co-pending application no. EP 0 458 472. In this case the container supports and separates the catalyst while providing the distillation surfaces for the distillation.

So far, the most commercially successful arrangement has been to place the particulate catalyst in closed pockets disposed along a fiber glass cloth belt as disclosed in US pat. no. 4,215,011.

EP-A-0 448 884, wich was filed on 27.12.90 with the priority of 30.03.90 and published on 02.10.91, discloses a catalytic distillation system comprising hollow mass transfer devices, for instance in the form of perforated balls or elongated geometric configurations, surrounded by a fixed catalytic bed comprising solid catalytic particles.

The main problems sought to be overcome by the improvements have been the reduction of pressure drop through the column and provision of sufficient contact of the reactants with the catalyst while providing for good vapor liquid contact for the fractional distillation. Many useful catalysts are in the form of fine particulate powders which preclude their use directly as distillation components. Even larger extruded pellets do not lend themselves well as distillation structures. Hence the use of cloth belts, cages and support trays is the predominate developmental thrust. While larger catalysts structures have been proposed, the porosity requirements of many catalytic materials limit their structural integrity. Many catalysts which rely on outer surface activity only and which might have the strength for larger structures are useful only for gas phase reactions, such as maleic anhydride production.

SUMMARY OF THE INVENTION

According to the present invention there is provided a catalytic distillation system for simultaneously carrying out chemical reactions ad fractional distillation of the products and reactants, comprising catalyst particles dispersed among hollow spacing elements, each of said hollow spacing elements having openings through the surface thereof, said openings being generally smaller than said catalyst particles, said particles being extrudates or spherical beads having a diameter of from 0.79 mm (1/32 mm inch) to 12.7 mm ($\frac{1}{2}$ inch).

The combined volume within the hollow spacing elements is preferably 50 per cent of the total volume of the catalyst particles and the hollow spacing elements. The catalyst component may comprise 40 to 70% of the total volume of the system.

The hollow spacing elements are preferably geometric components having openings therethrough over substantially the entire surface thereof, said hollow spacing elements preferably being intimately commingled with the catalyst particles.

The catalytic distillation system of the present invention is a dual component system. The first component is a particulate catalyst useful for carrying out the desired chemical reaction. The second component is a spacing element which is essentially a hollow geometric shape having openings through the outer surface to allow gas and liquid to pass therethrough. The two components are mixed to provide the desired open space and loaded into a distillation column reactor. The hollow geometric shapes provide the spacing, while the openings permit the gas and liquid to flow through, thus providing the requisite vapor liquid contact space and surfaces.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a depiction of a hollow spherical spacing element having slotted openings through the surface.

FIG. 2 is a depiction of a hollow spherical spacing element having circular openings through the surface.

FIG. 3 is a depiction of a hollow cylindrical spacing element having circular openings though the end surfaces and spiral slotted openings through the side surface.

FIG. 4 is a depiction of a hollow cylindrical spacing element having circular openings through the end and side surfaces.

FIG. 5 is a depiction of a hollow cylindrical spacing element having circular openings through the end surfaces and longitudinal slots through the side surface.

FIG. 6 is a depiction of the embodiment of either FIG. 1 or FIG. 2 as loaded into a distillation column reactor supporting and dispersing an extruded particulate catalyst.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention provides a catalytic distillation system in which particulate catalysts may be used without the special containers heretofore required. In order to provide both catalytic and distillation functions there are three highly desirable criteria. First, the system should be such as to provide for relatively even spatial dispersion in the distillation column reactor. That is, the catalyst system must rest in the column in a geometric arrangement which will perform the desired functions of reaction and distillation sites. To achieve this the system may be such as to provide fairly uniform spatial distribution in the column.

A second criteria is that there be sufficient free space in the catalyst bed to allow for the liquid phase contact and vapor phase distillation with the concurrent separation of the material in the column by the distillation into vapor and liquid phases. It has been observed that in the catalyst bed a free space of about 50 volume percent is adequate to obtain operable fractionation.

A third criteria is for the catalyst bed to be able to expand and contract during use without undue attrition of the catalyst.

These criteria are met by providing a spacing structure which may be used to disperse and support the particulate catalyst. The spacing structures are hollow to provide the necessary free space. The free space provided by the hollow structures is accessed by openings through the surface. This unique structure differs from solid support structures such as ceramic balls or glass beads in that the volume within the structure is accessible to the vapor and liquid.

The particular size and shape of the spacing structures may be selected from any that is convenient for loading or which provides the necessary random free space for the required volume of particulate catalyst. Depending upon the size, the spacing structures may be loaded into the distillation column reactor first and the catalyst added, or the two may be mixed and loaded concurrently. However, it is expected that the size of the spacing structures will be substantially smaller than the reactor into which they are loaded, e.g 1×10^{-7} to 7×10^{-5} the volume of conventional reactors into which they are placed.

A preferred embodiment for the spacing element is spherical because the loading volume of spheres is more easily predicted. Two versions of the spherical embodiment are shown in FIG. 1 and FIG. 2. In FIG. 1 the spherical spacing element 10 is shown to have slotted openings 15 through the surface. In FIG. 2 the openings are shown to be circular ports 14.

FIG.'s 3-5 depict alternative cylindrical spacing elements. The only difference between the spacing elements shown is the type of openings on the ends 11 and side of the cylinder.

The openings in any embodiment are preferably smaller than the particulate catalyst with which the spacing element is used to prevent the catalyst from entering and filling the hollow space. A practical limit to the size of the openings may be the pressure drop caused by the vapor and liquid

entering and leaving the hollow element. The particulate catalyst with which the spacing elements are used to make up the catalytic distillation system can be of any convenient size or shape as long as the particles do not enter and fill the free space within the spacing elements. It is anticipated that extruded particulate catalysts of from 0.79 to 12.7 mm (1/32 to 1/2 inch) in diameter, such as any of the alumina or alumina supported catalysts, would particularly benefit from the use of the spacing elements. Additionally the spherical catalyst having a diameter of between 0.79 and 12.7 mm (1/32 to 1/2 inch) would probably also benefit. FIG. 6 depicts a mixture of spherical spacing elements 10 and extruded particulate catalyst 20 supported within a distillation column reactor 1 by a screen 2.

The size of the spacing elements may be larger, smaller or equal to the particulate catalyst depending upon the size of the catalyst particles. The material for the spacing elements is preferably inert and should be rigid to maintain their integrity while being loaded and during operation. Additionally, the materials of construction must be able to withstand the environment within a distillation column reactor. Any of the various grades of stainless steel, ceramics, glass or some of the newer plastics which are available would be suitable depending upon the service.

Preferably the catalytic component will comprise 40 to 70% of the total volume of the system.

Claims

1. A catalytic distillation system for simultaneously carrying out chemical reactions and fractional distillation of the products and reactants, comprising catalyst particles dispersed among hollow spacing elements, each of said hollow spacing elements having openings through the surface thereof, said openings being generally smaller than said catalyst particles, said particles being extrudates or spherical beads having a diameter of from 0.79 mm (1/32 inch) to 12.7 mm ($\frac{1}{2}$ inch).

2. The catalytic distillation system of Claim 1 wherein said hollow spacing elements are larger than said particles.

3. The catalytic distillation system of Claim 1 wherein said hollow spacing elements are substantially the same size as said particles.

4. The catalytic distillation system of Claim 1 wherein said hollow spacing elements are smaller than said particles.

5. The catalytic distillation system of any one of Claims 1 to 4 wherein said hollow spacing elements are spherical in shape.

6. The catalytic distillation system of any one of Claims 1 to 4 wherein said hollow spacing elements are cylindrical in shape.

7. The catalytic distillation system of any one of Claims 1 to 6 wherein the combined volume within said hollow spacing elements is 50 per cent of the total volume of said catalyst particles and said hollow spacing elements.

8. The catalytic distillation system of any one of Claims 1 to 7 wherein the catalyst component comprises 40 to 70% of the total volume of the system.

9. A catalytic distillation system according to any one of Claims 1 to 8, wherein the hollow spacing elements are geometric components having openings therethrough over substantially the entire surface thereof, said hollow spacing elements being intimately commingled with the catalyst particles.

Patentansprüche

1. Katalytisches Destillationssystem zur gleichzeitigen Durchführung von chemischen Reaktionen und fraktionierten Destillationen von Produkten und Reaktionspartnern, welches zwischen hohlen Abstandhalterelementen dispergierte Katalysatorteilchen umfaßt, wobei jedes der hohlen Abstandhalterelemente Öffnungen durch seine Oberfläche hindurch aufweist, jene Öffnungen im allgemeinen kleiner als die Katalysatorteilchen sind und die Teilchen Extrudate oder kugelförmige Perlen mit einem Durchmesser von 0,79 mm (1/32 inch) bis 12,7 mm (1/2 inch) darstellen.

2. Katalytisches Destillationssystem gemäß Anspruch 1, bei welchem die hohlen Abstandhalterelemente größer als die Teilchen sind.

3. Katalytisches Destillationssystem gemäß Anspruch 1, bei welchen die hohlen Abstandhalterelemente im wesentlichen dieselbe Größe wie die Teilchen aufweisen.

4. Katalytisches Destillationssystem gemäß Anspruch 1, bei welchem die hohlen Abstandhalterelemente kleiner als die Teilchen sind.

5. Katalytisches Destillationssystem gemäß einem der Ansprüche 1 bis 4, bei dem die

hohlen Abstandhalterelemente Kugelform haben.

6. Katalytisches Destillationssystem gemäß einem der Ansprüche 1 bis 4, bei dem die hohlen Abstandhalterelemente in zylindrischer Form vorliegen.

7. Katalytisches Destillationssystem gemäß einem der Ansprüche 1 bis 6, bei welchem die kombinierten Volumina in den hohlen Abstandhalterelementen 50 Prozent des Gesamtvolumens von Katalysatorteilchen und hohlen Abstandhalterelementen ausmacht.

8. Katalytisches Destillationssystem gemäß einem der Ansprüche 1 bis 7, bei welchem die Katalysatorkomponente 40 bis 70 % des Gesamtvolumens des Systems ausmacht.

9. Katalytisches Destillationssystem gemäß einem der Ansprüche 1 bis 8, bei welchem die hohlen Abstandhalterelemente geometrische Komponenten mit im wesentlichen über ihre gesamte Oberfläche verteilten Öffnungen darstellen und bei welchem die hohlen Abstandhalterelemente innig mit den Katalysatorteilchen vermischt sind.

Revendications

1. Système de distillation catalytique pour exécuter, en même temps, des réactions chimiques et une distillation fractionnée des produits et des corps participant à la réaction, comprenant des particules de catalyseur dispersées parmi des éléments d'espacement creux, chacun desdits éléments d'espacement creux possédant des ouvertures sur la surface de celui-ci, lesdites ouvertures étant globalement plus petites que lesdites particules de catalyseur, lesdites particules étant des produits d'extrusion ou des perles sphériques ayant un diamètre compris entre 0,79 mm (1/32 de pouce) et 12,7 mm (1/2 pouce).

2. Système de distillation catalytique selon la revendication 1, dans lequel lesdits éléments d'espacement creux sont plus grands que lesdites particules.

3. Système de distillation catalytique selon la revendication 1, dans lequel lesdits éléments d'espacement creux ont sensiblement la même taille que lesdites particules.

4. Système de distillation catalytique selon la revendication 1, dans lequel lesdits éléments d'espacement creux sont plus petits que lesdites particules.

5. Système de distillation catalytique selon l'une quelconque des revendications 1 à 4, dans lequel lesdits éléments d'espacement creux sont de forme sphérique.

6. Système de distillation catalytique selon l'une quelconque des revendications 1 à 4, dans lequel lesdits éléments d'espacement creux sont de forme cylindrique.

7. Système de distillation catalytique selon l'une quelconque des revendications 1 à 6, dans lequel le volume combiné à l'intérieur desdits éléments d'espacement creux est de 50 pour cent du volume total desdites particules de catalyseur et desdits éléments d'espacement creux.

8. Système de distillation catalytique selon l'une quelconque des revendications 1 à 7, dans lequel la composante de catalyseur est constituée de 40 à 70 % du volume total du système.

9. Système de distillation catalytique selon l'une quelconque des revendications 1 à 8, dans lequel lesdits éléments d'espacement creux sont des composantes géométriques ayant des ouvertures traversantes sur sensiblement la totalité de leurs surfaces, lesdits éléments d'espacement creux étant intimement mélangés avec les particules de catalyseur.

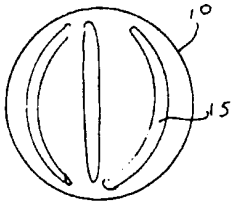

FIG. 1

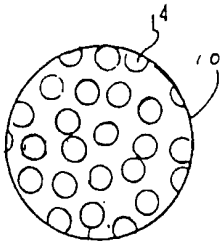

FIG. 2

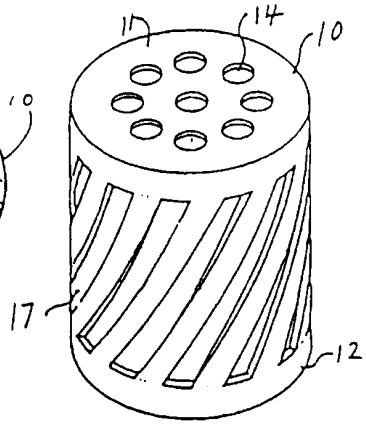

FIG. 3

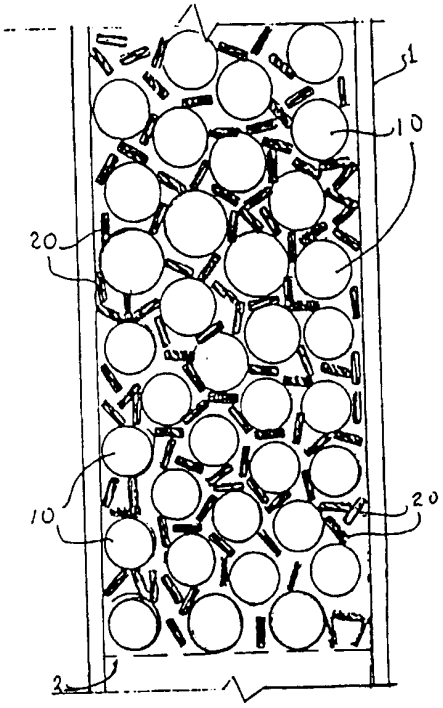

FIG. 6

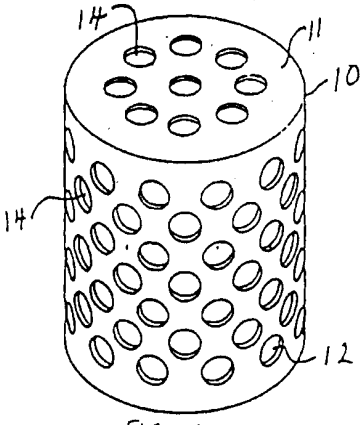

FIG. 4

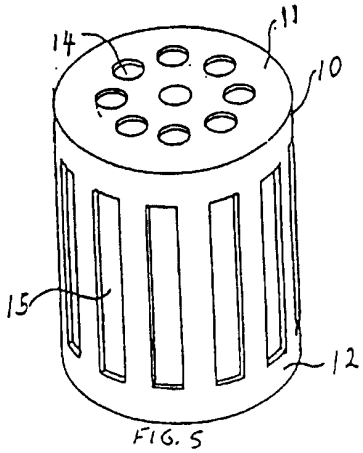

FIG. 5